

Measurements of NO₂, ΣPNs, ΣANs, and HNO₃ by Thermal Dissociation and Laser Induced Fluorescence during INTEX

Ronald C. Cohen

University of California, Berkeley

During INTEX, we will use thermal-dissociation coupled to laser-induced fluorescence (TD-LIF) detection of NO₂ for observations of NO₂, total peroxy nitrates (ΣPNs ≡ PAN + PPN + N₂O₅ + HNO₄ . . .), total alkyl- and hydroxyalkyl nitrates (ΣANs), HNO₃ and the sum of these four classes of NO_y species. Observations obtained via TD-LIF will be used to address questions pertaining to the source distribution and chemical speciation of NO_y in the Continental Boundary Layer (CBL), their export from the CBL to the free troposphere and their subsequent transport into the North Atlantic. ΣANs are routinely > 5% of NO_z in the boundary layer [Day et al., 2003; Rosen et al., 2004]. We will use chemical indicators such as the correlation between ΣANs and O₃ (Figure 1) to further our understanding of the competing effects of source strength and transport on ΣAN production. Additionally, correlations of NO_y, ΣANs, ΣPNs and NO₂ with CO will be useful in determining the export efficiency of various NO_y species under a wide variety of meteorological conditions. We have also previously used ΣPN measurements in combination with PAN and PPN to infer HNO₄ mixing ratios [Murphy et al., 2004]. Finally, we have the unique capability to observe both speciated NO_y classes alongside the sum of most oxidized nitrogen species (NO_y-NO) using a single technique. This will prove extremely useful as an internal cross check on the comparability of NO₂, PAN, HNO₄ and HNO₃ made by other investigators.

Instrumentation

NO₂ Detection

Briefly, the TD-LIF instrument we will fly aboard the DC-8 during INTEX uses a compact, diode pumped, Q-switched (10 kHz, 30nsec pulse length), frequency doubled (532nm), Nd³⁺: YAG laser to pump a tunable dye laser (500mW @ 585nm with a linewidth of 0.06 cm⁻¹) [Thornton et al., 2000]. The home-built, etalon tuned dye laser is used to tune the laser to excite a narrow rovibronic feature unique to NO₂. The light from the dye laser is focused sequentially into two 40 pass White cells. Red-shifted fluorescent photons at wavelengths longer than 700 nm are collected and imaged onto the photocathode of a cooled GaAs photomultiplier tube. Dichroic filters manufactured using

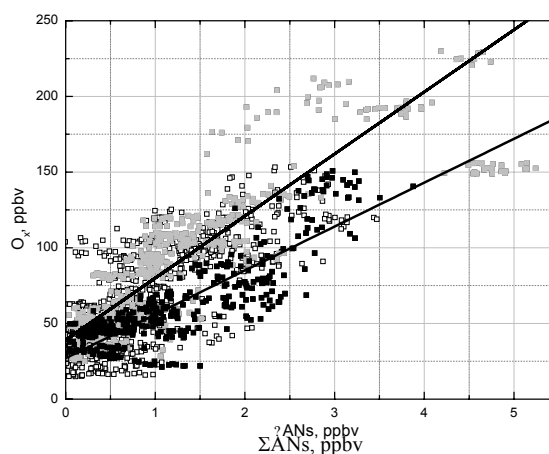


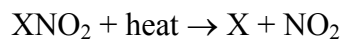
Figure 1. ΣANs vs. O₃ during August 2000 at La Porte, TX outside of Houston. Data from the AM are shown in black and from midafternoon in gray.

fused silica substrates and without any absorbing components are used to reject Rayleigh, Raman and chamber scatter. Single photons are counted using time-gated photon counting techniques. The laser is alternately tuned between a strong NO₂ resonance and the weaker continuum absorption to test for interferences, assess the background scattering, and for use in an algorithm that holds the laser frequency locked on a single spectral feature.

We incorporate a supersonic expansion in the detection region, increasing the population of NO₂ in the rotational state we excite [Cleary et al., 2002]. The gas sample flowing at 1SLM is expanded through a 0.3 μm pinhole into a chamber held at 250mtorr. The resulting rotational temperature in the jet is ~25K which enhances the signal by a factor of 30. The primary instrument calibration is the response to additions of NIST traceable NO₂ standards of 5-20 ppm diluted with zero air. The calibration is repeated as often as necessary to capture alignment changes or potential interferences from the atmosphere. We also frequently measure the instrument zero by over-pressuring the inlet with zero air. The detection sensitivity of this instrument is 0.8ppt/min at S/N=2. The uncertainty in the instrument zero is less than 1ppt.

ΣPN, ΣAN and HNO₃ detection

We couple a thermal dissociation pre-reactor to the LIF detector to observe ΣPNs, ΣANs and HNO₃ [Day et al., 2002]. These species thermally dissociate to yield NO₂ and a companion radical:



The sample is rapidly heated in a quartz tube, producing an enhancement in NO₂ over the ambient background. After flowing through a short region that allows the sample to cool to near ambient temperature, the sample is transported in PFA Teflon tubing to the LIF detection system where NO₂ is observed. At a residence time of 30-90ms and a pressure of 1 atmosphere, approximate temperatures for complete dissociation are: 200°C for ΣPNs; 400°C for ΣANs; and finally 650°C for HNO₃ (Figure 2).

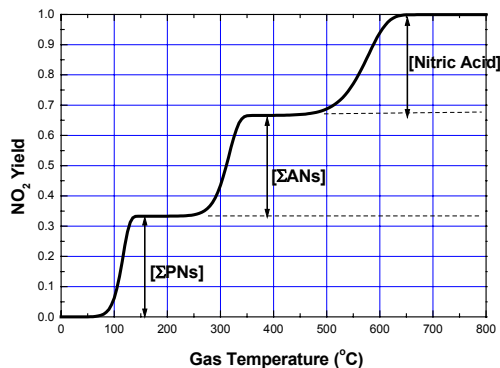


Figure 2. Theoretical yield of NO₂ from an equal mixture of 3 classes of nitrogen oxides.

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